

## Synthesis and Structural Characterization of a Novel $WRu_2$ Cluster Compound Possessing a Terminal Phenylimido Ligand

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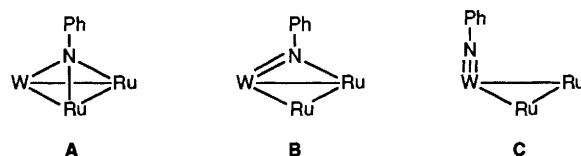
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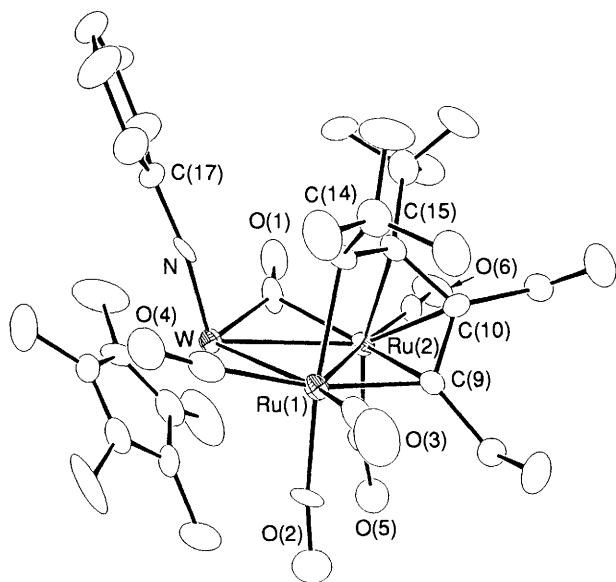
Cluster complex  $[WRu_2(C_5Me_5)(CO)_6(NPh)\{C(Et)C(Et)C(CF_3)CH(CF_3)\}]$  **2**, which possesses a novel terminal phenylimido ligand, has been prepared by treatment of phenylimido cluster  $[WRu_2(C_5Me_5)(CO)_7(\mu_3-NPh)(CF_3CCHCF_3)]$  **1** with hex-3-yne, whereas the respective reaction with dimethyl acetylenedicarboxylate afforded  $[WRu_2(C_5Me_5)(CO)_6(\mu_3-NPh)\{C(CO_2Me)C(CO_2Me)C(CF_3)CH(CF_3)\}]$  **3** containing a regular face-bridging imido ligand; complexes **2** and **3** have been examined by single-crystal X-ray diffraction.

There is considerable interest in the chemistry of cluster compounds containing an imido functional group.<sup>1</sup> The imido group is generally associated with the metal core *via* a typical  $\mu_3$ -mode<sup>1</sup> or a less common  $\mu_4$ -mode.<sup>2</sup> The  $\mu_3$ -mode was also observed in  $WRu_2$  cluster compounds, suggesting that the imido ligand has a tendency to interact with the metal skeleton *via* two M–N sigma bonds and an  $M \leftarrow N$  dative bond (mode **A**).<sup>3</sup> We are unaware of any example in which the imido ligand is coordinated to only one metal atom *via* a metal–nitrogen triple-bond (mode **C**), although a few examples of the asymmetric  $W=N(Ph) \rightarrow Ru$  mode in the related  $WRu_2$  system (mode **B**)<sup>4</sup> and the terminal mode in dinuclear complexes<sup>5</sup> have been documented. Now, we report the preparation and structural identification of the first example of mode **C**.

Treatment of the phenylimido complex  $[WRu_2(C_5Me_5)(CO)_7(\mu_3-NPh)(CF_3CCHCF_3)]$ <sup>3b</sup> **1** with an excess of hex-3-yne in refluxing toluene (100 °C, 30 min) afforded an alkyne–alkenyl coupling product  $[WRu_2(C_5Me_5)(CO)_6(NPh)\{C(Et)C(Et)C(CF_3)CH(CF_3)\}]$  **2** (46%). The formula was



Scheme 1



**Fig. 1** Molecular structure of **2** and the atomic numbering scheme. Selected bond lengths (Å): W–Ru(1) 2.933(1), W–Ru(2) 2.753(1), Ru(1)–Ru(2) 2.740(2), W–N 1.73(1); bond angle (°): W–N–C(17) 170.7(9).

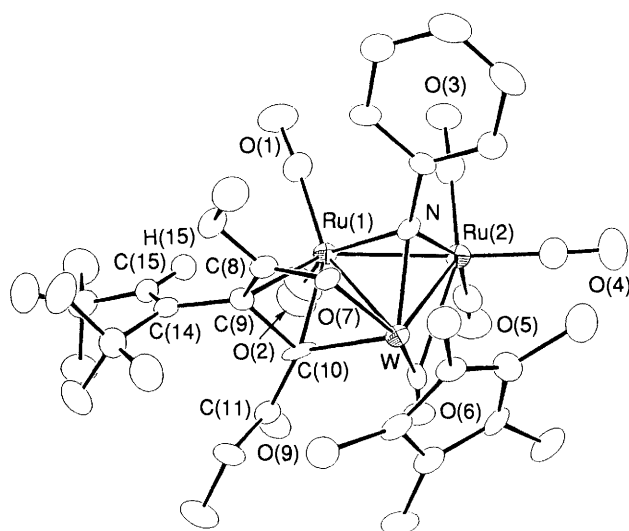
initially determined by mass, IR and NMR spectroscopy.† However, the key feature was provided by  $^{13}\text{C}$  NMR data, in which we observed that the *ipso*-carbon of the phenylimido group exhibited a large coupling to the tungsten atom ( $J_{\text{W,C}}$  40 Hz). These  $^2J_{\text{W,C}}$  coupling constants are greater than those of the  $\text{W}=\text{N}(\text{Ph})\rightarrow\text{Ru}$  imido ligands (21–24 Hz)<sup>3,4</sup> and are comparable to those of the mononuclear tungsten imido complexes,<sup>6</sup> suggesting the existence of an unusual terminal bonding mode. In order to establish the exact molecular structure, we carried out a single-crystal X-ray diffraction study of **2**.‡

Complex **2** consists of an isosceles  $\text{WRu}_2$  geometry (Fig. 1). The phenylimido ligand is coordinated to the tungsten atom with distance W–N 1.73(1) Å and angle W–N–C(17) 170.7(9)°. For comparison, the terminal  $\text{W}=\text{N}-\text{R}$  fragment in mononuclear complexes have W–N distances in the broad range 1.68–1.81 Å.<sup>7</sup> Furthermore, the butadienyl group, generated by insertion of alkyne into the *cis*-alkenyl fragment  $\text{CCF}_3=\text{CHCF}_3$ , is bridging the Ru(1)–Ru(2) edge with Ru–C distances in the range 2.21–2.12(1) Å. The stereochemistry of the alkenyl fragment is of interest because it has changed from *cis*- to *trans*-configuration with its hydrogen pointed towards the W atom to avoid steric congestion.

While complex **1** reacted with hex-3-yne to give a cluster with a terminal imido group, the reaction with dimethyl acetylenedicarboxylate afforded a  $\mu_3$ -imido cluster compound  $[\text{WRu}_2(\text{C}_5\text{Me}_5)(\text{CO})_6(\mu_3\text{-NPh})\{\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C}-$

† *Spectral data for 2*: MS (FAB,  $^{102}\text{Ru}$ ,  $^{184}\text{W}$ ),  $m/z$  1026( $\text{M}^+$ ). IR( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})/\text{cm}^{-1}$  2061s, 2032vs, 1997s, 1969s, 1958m, 1770m;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , room temp.):  $\delta$  7.18–7.13 (m, 3H), 6.95 (dd, 2H,  $J_{\text{H,H}}$  8.4 and 0.8 Hz), 3.13 (m, 1H), 3.10 (q, 1H,  $J_{\text{H,F}}$  12.0 Hz), 2.69 (m, 1H), 2.58 (m, 1H), 2.46 (m, 1H), 2.07 (s, 15H), 1.29 (t, 3H,  $J_{\text{H,H}}$  7.4 Hz), 1.18 (t, 3H,  $J_{\text{H,H}}$  7.6 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 253 K): CO,  $\delta$  277.4 ( $J_{\text{C,W}}$  162 Hz), 214.7, 209.8, 202.7, 200.0, 198.2;  $\delta$  155.2 (*i*- $\text{NC}_6\text{H}_5$ ,  $J_{\text{C,W}}$  40 Hz). Satisfactory C, H, N analyses were obtained.

‡ *Crystal data for 2*:  $\text{WRu}_2\text{C}_{33}\text{Cl}_2\text{F}_6\text{H}_{33}\text{NO}_6$ ,  $M = 1110.51$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 9.394(2)$ ,  $b = 19.291(3)$ ,  $c = 20.731(4)$  Å,  $V = 3757(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.964$  g cm<sup>−3</sup>,  $F(000) = 2144$ , Mo-K $\alpha$  radiation with  $\lambda = 0.70930$  Å,  $\mu(\text{Mo-K}\alpha) = 4.11$  mm<sup>−1</sup>. The min. and max. transmission factors are 0.856 and 1.000, 3712 unique reflections were measured, and 3404 reflections with  $I > 2\sigma(I)$  were used in refinement. Refinement of 84 atoms and 450 parameters converged to  $R_f = 0.044$  and  $R_w = 0.038$ , goodness of fit = 3.50.



**Fig. 2** Molecular structure of **3** and the atomic numbering scheme. Selected bond lengths (Å): W–Ru(1) 2.678(2), W–Ru(2) 2.861(1), Ru(1)–Ru(2) 2.667(1), W–N 2.010(7), Ru(1)–N 2.116(7), Ru(2)–N 2.035(7), Ru(1)–C(9) 2.316(9), Ru(1)–C(10) 2.093(9), W–C(10) 2.045(9), W–O(7) 2.199(5).

( $\text{CF}_3$ ) $\text{CH}(\text{CF}_3)$ ] **3** in 13% yield.§ The composition of this derivative, as indicated by FAB mass spectrometry, is closely related to that of **2**. However, the  $^{13}\text{C}$  NMR data indicate that the imido group adopts the  $\mu_3$ -mode because the *ipso*-carbon exhibits no obvious coupling to the tungsten. To confirm this, a single crystal X-ray diffraction study was performed.¶ As indicated in Fig. 2, complex **3** also has isosceles geometry. The phenylimido ligand sits on the  $\text{WRu}_2$  triangle; the Ru(1)–N distance (2.116 Å) differs from the other two [W–N 2.010 and Ru(2)–N 2.035 Å] by *ca.* 0.09 Å, which implies that the nitrogen atom is linked to Ru(1) and to Ru(2) and W atoms *via* a weak dative bond and regular  $\sigma$ -interactions, respectively. The butadienyl ligand forms a five-membered metallacycle and the  $\text{CCF}_3=\text{CHCF}_3$  fragment retains the original *cis*-configuration. From the view point of electron balancing, the coordination of the carboxylate oxygen atom O(7) to tungsten compensates the unsaturation caused by lifting the  $\pi$ -interaction of the  $\text{CCF}_3=\text{CHCF}_3$  fragment. Related metallacycles have been documented in the cluster compounds of acetamidoacrylic acid methyl ester<sup>8</sup> and of dialkyl fumarate.<sup>9</sup>

In summary, the phenylimido group can adopt three bonding modes in  $\text{WRu}_2$  clusters (Scheme 1). The formation of mode C is probably due to the unfavoured non-bonded steric interaction with the ligated butadienyl group,  $\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)$ . The contribution from the more

§ *Spectral data for 3*: MS (FAB,  $^{102}\text{Ru}$ ,  $^{184}\text{W}$ ),  $m/z$  1087( $\text{M}^+$ ). IR( $\text{CCl}_4$ ):  $\nu(\text{CO})/\text{cm}^{-1}$  2067vs, 2012s, 1994s, 1966m, 1952m, 1918vw, 1831w;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , room temp.):  $\delta$  7.12 (t, 2H,  $J_{\text{H,H}}$  7.2 Hz), 7.01 (t, 1H,  $J_{\text{H,H}}$  7.2 Hz), 6.82 (d, 1H,  $J_{\text{H,H}}$  8.0 Hz), 6.37 (q,  $J_{\text{H,F}}$  9.0 Hz), 3.66 (s, 3H), 3.62 (s, 3H), 1.85 (s, 15H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , room temp.): CO,  $\delta$  234.0 ( $J_{\text{C,W}}$  136 Hz), 208.4, 203.8, 195.3 (3C);  $\delta$  164.3 (*i*- $\text{NC}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , room temp.):  $\delta$  −56.78 (q, 3F,  $J_{\text{F,F}}$  11.2 Hz), −58.66 (m, 3F,  $J_{\text{F,F}}$  11.2,  $J_{\text{F,H}}$  9.1 Hz). Satisfactory C, H, N analyses were obtained.

¶ *Crystal data for 3*:  $\text{WRu}_2\text{C}_{32}\text{F}_6\text{H}_{27}\text{NO}_{10}$ ,  $M = 1085.54$ , monoclinic, space group  $P2_1/c$ ,  $a = 10.470(9)$ ,  $b = 19.243(7)$ ,  $c = 17.891(9)$  Å,  $\beta = 101.14(6)^\circ$ ,  $V = 3537(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.039$  g cm<sup>−3</sup>,  $F(000) = 2088$ , Mo-K $\alpha$  radiation with  $\lambda = 0.70930$  Å,  $\mu(\text{Mo-K}\alpha) = 4.23$  mm<sup>−1</sup>. The min. and max. transmission factors are 0.643 and 1.000, 4617 unique reflections were measured, and 3805 reflections with  $I > 2\sigma(I)$  were used in refinement. Refinement of 79 atoms and 470 parameters converged to  $R_f = 0.036$  and  $R_w = 0.030$ , goodness of fit = 2.95.

Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

electron-releasing  $C_5Me_5$  ligand<sup>10</sup> is also of importance, since treatment of the  $C_5H_5$  analogue of **1** with alkyne fails to afford any isolable cluster compound. In complex **3**, the generation of the metallacycle removes the electron deficiency of the tungsten centre *via* oxygen coordination, this permits the imido ligand to retain the original  $\mu_3$ -mode. The facile interconversion of the  $\mu_3$ -,  $\mu_2$ - and terminal modes implies that the imido group is able to move freely on the surface of  $WRu_2$  clusters, thus completely eliminating the possibility of using it as a 'protecting group' to prevent the unwanted fragmentation reaction<sup>11</sup> for clusters containing electropositive, early transition metal elements.

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